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Progress has been made in both experimentation and theoretical studies on chemical instabilities. Some measurements are reported on the dependence of the dynamics of the oscillatory combustion of acetaldehyde in a CSTR upon reactant input rates. Under our conditions, the period of the oscillation is found to be more strongly dependent upon the acetaldehyde input rate than the oxygen input rate. These results are compared with calculations made with a five-variable, twelve-step model. We have made extensive studies of the combustion of acetaldehyde under cool flame conditions in regions of external temperature of the reaction vessel, the pressure and stirring rates of the reacting mixture in the vessel. We have mapped out periodic, quasi periodic and chaotic regions of temporal variations of concentrations. We have carefully studied the problem of identification of chaos and have used a number of techniques including the power spectrum of the temporal variations of concentrations, correlation functions, distributions of periods of oscillations, and the so called Procaccia-Grassberger technique. Keyword

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FINAL REPORT

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Theory and Experiments on Chemical Instabilities

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Progress has been made in both experimentation and theoretical studies on chemical instabilities.

1. Combustion reactions under cool flame conditions. Effects of non-equimolar reactant flux on the oscillatory oxidation of acetaldehyde.

Some measurements are reported on the dependence of the dynamics of the oscillatory combustion of acetaldehyde in a CSTR upon reactant input rates. We map a kinetic phase diagram for the different types of behavior, stationary states and oscillations, found with non-equimolar input fluxes of acetaldehyde and oxygen. Hysteresis is observed in the transition from steady dark oxidation to oscillatory cool flames as the oxygen input flux is varied. We measure the dependence of the period and amplitude of the oscillatory cool flame light emission on both input fluxes. Under our conditions, the period of the oscillation is found to be more strongly dependent upon the acetaldehyde input rate than the oxygen input rate. These results are compared with calculations made with a five-variable, twelve-step model. This manuscript has been accepted for publication in the Journal of Physical Chemistry (216).

Periodic Quasi-Periodic and Chaotic Variations of Concentrations in Combustion Reactions.

We have made extensive studies of the combustion of acetaldehyde under cool flame conditions in regions of external temperature of the reaction vessel, the pressure and stirring rates of the reacting mixture in the vessel. We have mapped out periodic, quasi periodic and chaotic regions of temporal variations of concentrations. We have carefully studied the problem of identification of chaos and have used a number of techniques including the power spectrum of the temporal variations of concentrations, correlation functions, distributions of periods of oscillations, and the so called Procaccia-Grassberger technique. The presence of unavoidable experimental noise makes each one of the procedures suspect to doubt and proof of the presence of chaos requires a great deal of substantiation. Two articles on this work are in process of preparation for publication.

2. Effects of Time-Delay in Chemical Rate Processes.

Time delay processes in chemical kinetics occur naturally and can be imposed by means of a delayed feedback. We study the temporal evolution

of homogeneous chemical reaction mechanisms (the autonomous system)
describable by ordinary differential equations subjected to an imposed
time delay, a delayed feedback. A natural delay process can be decomposed
into analogous components. At short delays the delayed feedback is shown
to stabilize different types of unstable stationary states of the
autonomous systems, as well as induce bistability in a monostable system.
At longer delays transitions into chaos are predicted. First we study the
chaotic response of autonomous bistable systems which support only
stationary states. A recipe for finding chaos is given. Chaos occurs for a
small parameter range in which the delayed feedback repeatedly injects
trajectories into the neighborhood of one of the marginally stable points
of the autonomous system. Secondly, we consider the imposition of a
delayed feedback to a system in which periodic oscillations occur and
show that this leads to both chaos and hyperchaos when memory effects in
the delay cause the system to be reinjected into the neighborhood of a
saddle-focus point. The examples studied in detail are thermo-illuminated
chemical reactions, but we also consider the applicability of our results
to reactions in continuously stirred tank reactors and biochemical

processes. The results of this study show that natural time delays can regulate a wide range of dynamical behavior in biochemical processes. This work has been published in the Journal of Chemical Physics (210).

3. Experimental Studies on Chemical Waves

Experiments on Phase-Diffusion Waves.

Chemical waves are concentration profiles of reacting species which travel in space. Such waves occur in reactions with complex mechanism (autocalalysis, feed-back loop, etc) sufficiently far from equilibrium. Experiments have been made so far on two types of waves. 1. Kinematic waves result from imposed differences of concentrations (or other state variables), that is imposed phase differences or imposed differences in frequency, in oscillatory reactions. By definition, kinematic waves do not involve diffusion of species or heat. 2. Trigger waves in oscillatory or excitable reaction systems usually consist in part of sharp concentration profiles combined with more gradual variations of concentrations. These waves are described by partial differential equations which include reaction and diffusion. Both types of waves have been analyzed theoretically in some detail. In this work we present experiments on yet

another type of wave, predicted in 1973, which we shall call here a phase diffusion wave.

We can give a simple picture of phase diffusion waves. Consider an oscillatory reaction occuring homogeneously in a vessel (not stirred). By means of a perturbation such as the immersion of a catalyst at one point in the reacting solution in the vessel, we accelerate the overall rate of the reaction at that point, compared to the immediate neighborhood of that point. Due to this difference in the reaction rates, there are established differences in concentrations or differences in the phase of oscillation. The concentrations differences over given distances bring about diffusion and then phase diffusion occurs. If the oscillatory reaction system can have trigger or relaxation oscillation waves, then such waves occur if the perturbation is sufficiently large.

An oscillatory system in which there are imposed gradients of phase (or frequency) shows kinematic waves at small times after the imposition of the gradient because, for small times, the difference in concentrations of neighboring regions are small and then, for such times, diffusion plays a negligible role. However, as time proceeds, diffusion becomes important

and phase diffisuion occurs. It is useful to summarize the characteristics and operational distinctions among the three types of waves. Kinematic waves are not influenced by diffusion and, hence, are not stopped by barriers to diffusion. The distinctions between trigger waves and phase diffusion waves are: 1. The shape of the wave; trigger waves have steep gradient, phase diffusion waves do not, 2. The velocity of the wave: trigger waves have considerably smaller velocity than phase diffusion waves; the velocity of phase diffusion waves increases with decreasing phase gradient and it has no upper limit. 3. The limited range of constant velocity: trigger waves have a constant velocity in a range of distance of the order of the product of the velocity of the wave times the period of the oscillation. Phase diffusion waves have a range of constant velocity of the order of the square root of the product of the appropriate diffusion coefficient times the time elapsed since initiation of the experiment.

The oscillatory Belousov-Zhabotinsky reaction is perturbed inhomogeneously by illumination with a focused laser beam for a given time interval and a quantity of heat is thus produced in a small region. The perturbation initiates a trigger wave for larger laser power. As the

heat diffuses away from the initial location, the character of waves generated in succeeding cycles of the oscillatory reaction changes in a continuous manner to phase diffusion waves, predicted some years ago and observed for the first time. We measure transmission profiles with a Reticon system and calculate velocity profiles from the measurements. Phase shifts induced by the perturbation depend on the phase of the unperturbed oscillatory system at the instant of the imposition of the perturbation. For small perturbations, phase diffusion waves are induced initially. If the perturbation produces phase shifts exceeding 2π, then more than one trigger wave is generated within the first cycle of oscillation following the perturbation. A simple chemical model of oscillating reaction is used to calculate the major effects seen in the experiment.

This work has been accepted for publication in the Journal of Chemical Physics (217).

Measurement of Dispersion Relations of Chemical Waves in an Oscillatory Reacting Medium

We have measured the dispersion relation, that is the dependence and velocity of a chemical wave on the period of that wave, in the Belousov-Zhabotinsky reaction under conditions with a reacting solution as relaxation oscillations. This work is in preparation for publication in the Journal of Physical Chemistry.

4. Measurements and a Hypothesis on Periodic Percipitation Processes.

We report measurements on periodic precipitation processes in lead iodide with initial concentration gradients of electrolytes: by means of adsorption and reticon techniques, microscope observations and standard analytical methods we measure temporal developments of band formation (total precipitate), propagation of the precipitation front, spatial distribution of total iodide concentration, spatial distribution of particle number density, variation of average particle radius with spatial location in the system and particle size distributions. Structure formation occurs

also in directions in which there are no initial concentration gradients and we follow the temporal and spatial development of such structures by microscope photography A simple model of reaction, diffusion and nucleation correlates the measurements with initial concentration gradients, the Ostwald supersaturation model holds provided that the rate of nucleation is sufficiently sensitive to the degree of supersaturation. We offer a hypothesis of sequence of events leading to structure formation in directions with no initial gradients Such structures are formed due to the establishment of ion concentration gradients around a few randomly distributed particles in correspondence with observation. This work is being prepared for publication in the Journal of Chemical Physics

Invited Lectures

University of California, San Diego
Argonne National Laboratory
Canadian Conference on Theoretical Chemistry, Toronto
Symposium on Lasers, Molecules and Methods, Los Alamos
Symposium on Self-Organization, U.C. California, San Diego

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Submitted for Publication

*217. "Experiments on Phase Diffusion Waves," J. Chem. Phys., J. M. Bodet, J. Ross, and C. Vidal.

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